



(19)

Europäisches Patentamt
European Patent Office
Office européen des brevets



(11)

EP 1 191 090 A2

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:
27.03.2002 Bulletin 2002/13

(51) Int Cl.⁷: **C10M 169/04**
// (C10M101/02, 129:72,
143:04, 143:06, 143:08, 143:08,
143:12)

(21) Application number: **01307992.6**

(22) Date of filing: **19.09.2001**

(84) Designated Contracting States:
AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU
MC NL PT SE TR
Designated Extension States:
AL LT LV MK RO SI

(30) Priority: **19.09.2000 US 665568**

(71) Applicant: **ETHYL CORPORATION**
Richmond, Virginia 23219-4304 (US)

(72) Inventor: **Balasubramanian, Vasudevan**
Montpellier, Virginia 23192 (US)

(74) Representative: **Cresswell, Thomas Anthony**
J.A. Kemp & Co.
14 South Square
Gray's Inn
London WC1R 5LX (GB)

(54) **Gear oil formulations having enhanced performance**

(57) A lubricant composition suitable for use as an
automotive or industrial gear lubricant comprising:

(A) from about 40 to about 70 wt. %, based on the
total weight of the lubricant composition, of a min-
eral oil;

(B) from about 2 to about 20 wt. %, based on the
total weight of the lubricant composition, of at least
one selected from vinyl aromatic-diene copolymers,
olefin copolymers and mixtures thereof;

(C) from about 2 to about 20 wt. %, based on the
total weight of the lubricant composition, of at least
one polyalphaolefin having a kinematic viscosity of

at least 40 cSt at 100°C; and

(D) from about 3 to about 20 wt. %, based on the
total weight of the lubricant composition, of a gear
additive package;

wherein the lubricant composition has a Viscosity Index
of greater than 140.

EP 1 191 090 A2

Description**TECHNICAL FIELD**

- 5 **[0001]** The present invention relates to novel gear oil formulations containing specific combinations of viscosity index improvers and having excellent low and high temperature rheology as well as high axle efficiencies and low axle sump temperatures.

BACKGROUND INFORMATION

- 10 **[0002]** The primary function of a gear lubricant is to provide a high degree of reliability and durability in the service life of gear equipment. Gear lubricants may also contribute to improving the fuel economy of vehicles by improving the axle efficiency. See, for example, O'Connor et al., *The Relationship Between Laboratory Axle Efficiency and Vehicle Fuel Consumption* (SAE Paper No. 811206).
- 15 **[0003]** In the paper by O'Connor et al., entitled *Axle Efficiency - Response to Synthetic Lubricant Components* (SAE Paper No. 821181), the authors state that "[i]nvestigations with both partial- and full-synthetic base formulations have shown improvements compared to conventional petroleum base gear oils. Maximum benefits are gained with total synthetic base type formulations." The O'Connor paper fails to teach the advantages obtained by the petroleum based gear oil formulations of the present invention.
- 20 **[0004]** U.S. Patent No. 4,370,247 discloses a semi-synthetic gear and axle oil composition comprising (a) 5 to 50 mass % of a conventional gear/axle grade mineral oil; (b) 5 to 30 mass % of a polyoxyalkylene glycol; and (c) 25 to 60 mass % of at least one di-C₈ to C₁₂ alkyl ester of a dicarboxylic acid. The '247 patent fails to teach or reasonably suggest the petroleum based gear oil formulations of the present invention.
- 25 **[0005]** EP 790294 A2 discloses lubricating compositions comprising from about 5 to about 30% by weight of at least one polymer having a Mw less than 10,000 and from about 2 to about 12% by weight of a polymer having a Mw greater than about 15,000. The '294 reference does not teach the use of high viscosity polyalphaolefins in combination with olefin copolymers or the improvements obtained in axle efficiency and reduced axle temperatures obtained by using such a combination.

SUMMARY OF THE INVENTION

[0006] The present invention is directed to a gear oil composition comprising:

- 35 (A) a mineral oil;
 (B) at least one member selected from the group consisting of vinyl aromatic-diene copolymers, olefin copolymers and mixtures thereof;
 (C) at least one polyalphaolefin having a kinematic viscosity of at least 40 cSt at 100°C; and
 (D) a gear additive package.

- 40 **[0007]** The gear oil formulations of the present invention exhibit excellent low and high temperature rheology as well as higher axle efficiencies and lower axle sump temperatures compared to mineral oil-based gear formulations containing other viscosity index improvers.

DETAILED DESCRIPTION OF THE INVENTION

- 45 **[0008]** The present invention is directed to a gear oil composition comprising:

- (A) from about 40 to about 70 weight percent (wt. %), based on the total weight of the gear oil composition, of a mineral oil;
 50 (B) from about 2 to about 20 wt. %, based on the total weight of the gear oil composition, of at least one member selected from the group consisting of vinyl aromatic-diene copolymers, olefin copolymers and mixtures thereof;
 (C) from about 2 to about 20 wt. %, based on the total weight of the gear oil composition, of at least one polyalphaolefin having a kinematic viscosity of at least 40 cSt at 100 °C; and
 55 (D) from 3 to 20 wt. %, based on the total weight of the gear oil composition, of a gear additive package;

wherein the fully formulated gear oil composition has a Viscosity Index of greater than 140.

[0009] The mineral oil (A) of the present invention may be any mineral oil. In a preferred embodiment, the mineral oil is a hydrotreated, hydrocracked and/or iso-dewaxed mineral oil having a Viscosity Index of greater than 80, prefer-

ably greater than 90; greater than 90 volume % saturates and less than 0.03 wt. % sulfur.

[0010] The American Petroleum Institute has categorized basestock types as follows: Group I, >0.03 wt. % sulfur, and/or <90 vol% saturates, viscosity index between 80 and 120; Group II, ≤ 0.03 wt. % sulfur, and ≥ 90 vol% saturates, viscosity index between 80 and 120; and Group III, ≤ 0.03 wt. % sulfur, and ≥ 90 vol% saturates, viscosity index > 120.

5 Group II and Group III basestocks are particularly suitable for use in the present invention, and are typically prepared from conventional feedstocks using a severe hydrogenation step to reduce the aromatic, sulfur and nitrogen content, followed by dewaxing, hydrofinishing, extraction and/or distillation steps to produce the finished base oil. Group II and III basestocks differ from conventional solvent refined Group I basestocks in that their sulfur, nitrogen and aromatic contents are very low. As a result, these base oils are compositionally very different from conventional solvent refined basestocks. Blends of Group I, Group II and/or Group III base oils may also be used as Component A of this invention.

10 [0011] There is no limitation as to the chemical composition of the various basestocks used. For example, the proportions of aromatics, paraffinics, and naphthenics in the various Group I, Group II and Group III oils can vary substantially. This composition is generally determined by the degree of refining and the source of the crude used to produce the oil.

15 [0012] Component (B) of the present invention comprises at least one member selected from the group consisting of vinyl aromatic-diene copolymers, olefin copolymers and mixtures thereof.

[0013] The vinyl aromatic-diene copolymers particularly suitable for the present invention include hydrogenated diene/vinyl aromatic diblock and triblock copolymers. These copolymers are typically prepared from, first, a vinyl aromatic monomer. The aromatic portion of this monomer can comprise a single aromatic ring or a fused or multiple aromatic ring. 20 Examples of fused or multiple aromatic ring materials include vinyl substituted naphthalenes, anthracenes, phenanthrenes and biphenyls. The aromatic comonomer may also contain one or more heteroatoms in the aromatic ring, provided that the comonomer substantially retains its aromatic properties and does not otherwise interfere with the properties of the polymer. Suitable heteroaromatic materials include vinyl-substituted thiophene, 2-vinylpyridine, 4-vinylpyridine, N-vinylcarbazole and N-vinylloxazole. Preferably, the monomers are styrenes such as styrene, alpha-methyl styrene, ortho-methyl styrene, meta-methyl styrene and para-methyl styrene. Most preferably, the vinyl aromatic monomer is styrene. The vinyl group in the vinyl aromatic monomer is preferably an unsubstituted vinyl (e.g., $\text{CH}_2=\text{CH}-$) group, or an equivalent group of such a nature that it provides adequate means of incorporation of the aromatic comonomer into the polymer chain as a "block" of homopolymer, having a number of consecutive uniform repeating units, which imparts a high degree of aromatic content to the block.

30 [0014] The dienes suitable for preparing the block copolymers of the present invention contain two double bonds, commonly located in conjugation in a 1,3 relationship. Olefins containing more than two double bonds, sometimes referred to as polyenes, are also considered to be within the definition of "dienes" as used herein. Examples of such diene monomers include 1,3-butadiene as well as hydrocarbyl-substituted butadienes such as isoprene and 2,3-dimethylbutadiene. Mixtures of such conjugated dienes are also useful.

35 [0015] The vinyl aromatic content of the copolymers is typically in the range of about 20% to about 70% by weight, preferably about 40% to about 60% by weight. The remaining comonomer content of these copolymers is typically in the range of about 30% to about 80% by weight, preferably about 40% to about 60% by weight. Additional monomers may also be present, normally in relatively small amounts (e.g., about 5 to about 20 percent). These additional monomers include C_{2-10} olefin oxides, caprolactone and butyrolactone.

40 [0016] The di- and tri-block copolymers useful in the present invention are preferably made by anionic polymerization, using a variety of techniques and altering reaction conditions to produce the desired features in the resulting copolymer. Hydrogenation of the unsaturated block polymers produces polymers that are more oxidatively and thermally stable. Hydrogenation is typically carried out as part of the polymerization process, using finely divided, or supported, nickel catalyst. Other transition metals may also be used to effect the transformation. Hydrogenation is normally carried out to reduce at least about 94% of the olefinic unsaturation of the initial polymer. In general, it is preferred that these copolymers, for reasons of oxidative stability, contain no more than about 5% and more preferably no more than about 0.5% residual olefinic unsaturation on the basis of the total amount of olefinic double bonds present in the polymer prior to hydrogenation. Such unsaturation can be measured by a number of means well known to those skilled in the art, such as infrared or nuclear magnetic resonance spectroscopy. Most preferably, these copolymers contain no discernible unsaturation, as determined by the aforementioned analytical techniques.

50 [0017] The polymers, and in particular styrene-diene copolymers, are, in a preferred embodiment, block copolymers in which a portion of the blocks are composed of homopolymer or homo-oligomer segments of the vinyl aromatic monomer and another portion of the blocks are composed of homopolymer or homo-oligomer segments of the diene monomer. The polymers generally possess a number average molecular weight of at least 50,000, preferably at least 100,000. Generally, the polymers should not exceed a number average molecular weight of 500,000 preferably 300,000. The number average molecular weight for such polymers is determined by gel permeation chromatography (GPC). The molecular weight and the amount of polymer used should be selected such that the formulated oil will not shear out of grade according to SAE J306 requirements when subjected to the 20-hour taper bearing shear test

(CEC-L45-T-93).

[0018] Suitable styrene/isoprene hydrogenated regular diblock copolymers are available commercially from Shell Chemical Co. under the trade names Shellvis™ 40 and Shellvis™ 50. Suitable styrene/1,3-butadiene hydrogenated random block copolymers are available from BASF under the trade name Glissoviscal™.

[0019] The vinyl aromatic-diene copolymers particularly suitable for the present invention also include star polymers. Star polymer are polymers comprising a nucleus and polymeric arms. Common nuclei include polyalkenyl compounds, usually compounds having at least two non-conjugated alkenyl groups, usually groups attached to electron withdrawing groups, e.g., aromatic nuclei. The polymeric arms are copolymers of conjugated dienes and vinyl aromatic compounds.

[0020] The star polymers are typically hydrogenated such that at least 80%, preferably at least 95%, of the covalent carbon-carbon double bonds are saturated. The polyvinyl compounds making up the nucleus are illustrated by polyalkenyl arenes, e.g., divinyl benzene and poly vinyl aliphatic compounds. Star polymers are commercially available, for example as Shellvis™ 200 sold by Shell Chemical Co.

[0021] The olefin copolymers particularly suitable for the present invention are ethylene-alphaolefin copolymers comprising ethylene and one or more alpha-olefins of the formula $H_2C=CHR$ wherein R is a hydrocarbon radical of from 1 to 10 carbon atoms. The copolymer-forming monomers can optionally include a nonconjugated polyene. Preferred alpha-olefins include propylene, 1-butene, 1-pentene, 1-hexene, 3-methyl pentene, 1-heptene, 1-octene and 1-decene. The optional nonconjugated polyenes include aliphatic dienes such as 1,4-hexadiene, 1,5-hexadiene, 1,4-pentadiene, 2-methyl-1,4-pentadiene, 3-methyl-1,4-hexadiene, 4-methyl-1,3-hexadiene, 1,9-decadiene, and exo- and endo-dicyclopentadiene; exo- and endo-alkenyl norbornenes such as 5-propenyl-, 5-(buten-2-yl)- and 5-(2-methylbuten-[2']-yl) norbornene; alkylalkenyl norbornenes such as 5-methyl-6-propenyl norbornene; alkylidenenorbornenes such as 5-methylene, 5-ethylidene and 5-isopropylidene-2-norbornene, vinyl norbornene and cyclohexyl norbornene; alkyl norbornadienes such as methyl-, ethyl- and propyl norbornadiene; and cycloolienes such as 1,5-cyclooctadiene and 1,4-cyclooctadiene.

[0022] The ethylene content of the olefin copolymers is generally from about 35 to about 65, and most preferably from about 40 to 60, weight percent. When present, the nonconjugated polyene generally ranges from about 0.01 to about 1, preferably from about 0.05 to about 0.5, and most preferably from about 0.1 to about 0.3, weight percent. The balance of the copolymers, for a total of 100 weight percent, is made up of alpha-olefins other than ethylene.

[0023] The olefin copolymers can be prepared in accordance with known procedures employing Ziegler-Natta catalysts or metallocene catalysts. The olefin copolymers generally possess a number average molecular weight (M_n) of from about 250 to about 50,000, preferably from about 1,000 to about 30,000. The molecular weight and the amount of polymer used should be selected such that the formulated oil will not shear out of grade according to SAE J306 requirements when subjected to the 20-hour taper bearing shear test (CEC-L45-T-93).

[0024] Component (C) comprises at least one high viscosity polyalphaolefin having a kinematic viscosity (KV) of at least 40 cSt, preferably from 40 to 3000 cSt, as measured at 100 °C according to ASTM D-445. The high viscosity polyalphaolefins may be prepared by any of a series of methods described in the literature. The catalysts employed include those commonly referred to as Friedel-Crafts catalysts. Such catalysts cause cationic oligomerization of alphaolefins, such as 1-octene and 1-decene, to molecular weights ranging up to several thousand depending on the catalyst and the polymerization conditions employed.

[0025] Ziegler catalysts, such as those described in U.S. Patent No. 3,179,711 to Sun Oil Company, can also be used to prepare oligomers in the molecular weight range useful in the present invention.

[0026] Polyalphaolefins can likewise be prepared with peroxide catalysts, BF_3 based catalysts and by thermal polymerization. These methods, however, generally only produce low molecular weight oligomers.

[0027] The high viscosity polyalphaolefins of this invention are preferably hydrogenated to decrease their level of unsaturation and thereby increase their stability toward oxidation.

[0028] The alpha-olefins utilized to make the high viscosity oligomers of the present invention can range from C_3 - C_{14} or any mixtures thereof, although oligomers of octene-1, decene-1 and dodecene-1 are preferred because of their high Viscosity Indices and low pour points.

[0029] Some additive components are supplied in the form of solutions of active ingredient(s) in an inert diluent or solvent, such as a diluent oil. Unless expressly stated to the contrary, the amounts and concentrations of each additive component are expressed in terms of active additive, i.e., the amount of solvent or diluent that may be associated with such component as received is excluded.

[0030] The gear additive package useful as component (C) in the present invention typically contains one or more additives selected from the group consisting of dispersants, corrosion inhibitors, extreme pressure additives, anti-wear additives, rust inhibitors, antioxidants, deodorizers, defoamers, demulsifiers, dyes, friction modifiers other than component (B) and fluorescent coloring agents. The gear additive package may be, although it does not have to be, a fully-formulated gear additive package, such as a package meeting the requirements for API GL-5 and/or API MT-1 and/or MIL-PRF-2105E and/or AGMA 9005-D94. The type and amount of the components present in the gear additive package will depend on the intended final use of the product.

[0031] The gear additive package is typically present in an amount of from about 2 to about 25 weight percent, based on the total weight of the lubricating oil composition.

[0032] The dispersants useful in the present invention comprise at least one oil-soluble ashless dispersant having a basic nitrogen and/or at least one hydroxyl group in the molecule. Suitable dispersants include alkenyl succinimides, alkenyl succinic acid esters, alkenyl succinic ester-amides, Mannich bases, hydrocarbyl polyamines, or polymeric polyamines.

[0033] The alkenyl succinimides in which the succinic group contains a hydrocarbyl substituent containing at least 30 carbon atoms are described for example in U.S. Pat. Nos. 3,172,892; 3,202,678; 3,216,936; 3,219,666; 3,254,025; 3,272,746; and 4,234,435. The alkenyl succinimides may be formed by conventional methods such as by heating an alkenyl succinic anhydride, acid, acid-ester, acid halide, or lower alkyl ester with a polyamine containing at least one primary amino group. The alkenyl succinic anhydride may be made readily by heating a mixture of olefin and maleic anhydride to, for example, about 180-220 °C. The olefin is preferably a polymer or copolymer of a lower mono-olefin such as ethylene, propylene, 1-butene, isobutene and the like and mixtures thereof. The more preferred source of alkenyl group is from polyisobutene having a gel permeation chromatography (GPC) number average molecular weight of up to 10,000 or higher, preferably in the range of about 500 to about 2,500, and more preferably in the range of about 800 to about 1,500.

[0034] As used herein the term "succinimide" is meant to encompass the completed reaction product from reaction between one or more polyamine reactants and a hydrocarbon-substituted succinic acid or anhydride (or like succinic acylating agent), and is intended to encompass compounds wherein the product may have amide, amidine, and/or salt linkages in addition to the imide linkage of the type that results from the reaction of a primary amino group and an anhydride moiety.

[0035] The various types of ashless dispersants described above can be phosphorylated by procedures described in U.S. Patent Nos. 3,184,411; 3,342,735; 3,403,102; 3,502,607; 3,511,780; 3,513,093; 4,615,826; 4,648,980; 4,857,214 and 5,198,133.

[0036] The dispersants of the present invention may be boronated. Methods for boronating (borating) the various types of ashless dispersants described above are described in U.S. Pat. Nos. 3,087,936; 3,254,025; 3,281,428; 3,282,955; 2,284,409; 2,284,410; 3,338,832; 3,344,069; 3,533,945; 3,658,836; 3,703,536; 3,718,663; 4,455,243; and 4,652,387.

[0037] Preferred procedures for phosphorylating and boronating ashless dispersants such as those referred to above are set forth in U.S. Pat. Nos. 4,857,214 and 5,198,133.

[0038] The amount of ashless dispersant, when present, on an "active ingredient basis" (i.e., excluding the weight of impurities, diluents and solvents typically associated therewith) is generally within the range of about 0.5 to about 7.5 weight percent (wt%), typically within the range of about 0.5 to 5.0 wt%, preferably within the range of about 0.5 to about 3.0 wt%, and most preferably within the range of about 2.0 to about 3.0 wt%, based on the finished oil.

[0039] The lubricant compositions of the present invention typically will contain some inhibitors. The inhibitor components serve different functions including rust inhibition, corrosion inhibition and foam inhibition. The inhibitors may be introduced in a pre-formed additive package that may contain in addition one or more other components used in the compositions of this invention. Alternatively these inhibitor components can be introduced individually or in various sub-combinations. While amounts can be varied within reasonable limits, the finished fluids of this invention will typically have a total inhibitor content in the range of about 0 to about 10 wt%, on an "active ingredient basis", i.e., excluding the weight of inert materials such as solvents or diluents normally associated therewith.

[0040] Foam inhibitors form one type of inhibitor suitable for use as inhibitor components in the compositions of this invention. These include silicones, polyacrylates, surfactants, and the like.

[0041] Copper corrosion inhibitors constitute another class of additives suitable for inclusion in the compositions of this invention. Such compounds include thiazoles, triazoles and thiadiazoles. Examples of such compounds include benzotriazole, tolyltriazole, octyltriazole, decyltriazole, dodecyltriazole, 2-mercapto benzothiazole, 2,5-dimercapto-1,3,4-thiadiazole, 2-mercapto-5-hydrocarbylthio-1,3,4-thiadiazoles, 2-mercapto-5-hydrocarbyldithio-1,3,4-thiadiazoles, 2,5-bis(hydrocarbylthio)-1,3,4-thiadiazoles, and 2,5-bis(hydrocarbyldithio)-1,3,4-thiadiazoles. The preferred compounds are the 1,3,4-thiadiazoles, a number of which are available as articles of commerce, and also combinations of triazoles such as tolyltriazole with a 1,3,5-thiadiazole such as a 2,5-bis(alkyldithio)-1,3,4-thiadiazole. Materials of these types that are available on the open market include Cobratex™ TT-100 and HITEC® 314 additive and HITEC® 4313 additive (Ethyl Petroleum Additives, Inc.). The 1,3,4-thiadiazoles are generally synthesized from hydrazine and carbon disulfide by known procedures. See, for example, U.S. Pat. Nos. 2,765,289; 2,749,311; 2,760,933; 2,850,453; 2,910,439; 3,663,561; 3,862,798; and 3,840,549.

[0042] Rust or corrosion inhibitors comprise another type of inhibitor additive for use in this invention. Such materials include monocarboxylic acids and polycarboxylic acids. Examples of suitable monocarboxylic acids are octanoic acid, decanoic acid and dodecanoic acid. Suitable polycarboxylic acids include dimer and trimer acids such as are produced from such acids as tall oil fatty acids, oleic acid, linoleic acid, or the like. Products of this type are currently available

from various commercial sources, such as, for example, the dimer and trimer acids sold under the HYSTRENE trademark by the Humko Chemical Division of Witco Chemical Corporation and under the EMPOL trademark by Henkel Corporation. Another useful type of rust inhibitor for use in the practice of this invention is comprised of the alkenyl succinic acid and alkenyl succinic anhydride corrosion inhibitors such as, for example, tetrapropenylsuccinic acid, tetrapropenylsuccinic anhydride, tetradecenylsuccinic acid, tetradecenylsuccinic anhydride, hexadecenylsuccinic acid, hexadecenylsuccinic anhydride, and the like. Also useful are the half esters of alkenyl succinic acids having 8 to 24 carbon atoms in the alkenyl group with alcohols such as the polyglycols. Other suitable rust or corrosion inhibitors include ether amines; acid phosphates; amines; polyethoxylated compounds such as ethoxylated amines, ethoxylated phenols, and ethoxylated alcohols; imidazolines; aminosuccinic acids or derivatives thereof, and the like. Materials of these types are available as articles of commerce. Mixtures of such rust or corrosion inhibitors can be used.

[0043] Antioxidants may also be present in the lubricant formulations of the present invention. Suitable antioxidants include phenolic antioxidants, aromatic amine antioxidants, sulfurized phenolic antioxidants, and organic phosphites, among others. Examples of phenolic antioxidants include 2,6-di-tert-butylphenol, liquid mixtures of tertiary butylated phenols, 2,6-di-tert-butyl-4-methylphenol, 4,4'-methylenebis(2,6-di-tert-butylphenol), 2,2'-methylenebis(4-methyl-6-tert-butylphenol), mixed methylene-bridged polyalkyl phenols, and 4,4'-thiobis(2-methyl-6-tert-butylphenol). N,N'-di-sec-butyl-p-phenylenediamine, 4-isopropylaminodiphenyl amine, phenyl-naphthyl amines, and ring-alkylated diphenylamines serve as examples of aromatic amine antioxidants. Preferred are the sterically hindered tertiary butylated phenols, the ring alkylated diphenylamines and combinations thereof.

[0044] The amounts of the inhibitor components used will depend to some extent upon the composition of the component and its effectiveness when used in the finished composition. However, generally speaking, the finished fluid will typically contain the following concentrations (weight percent) of the inhibitor components (active ingredient basis):

Inhibitor	Typical Range	Preferred Range
Foam inhibitor	0 to 0.2	0.01 to 0.08
Copper corrosion inhibitor	0 to 3	0.01 to 1
Rust inhibitor	0 to 3	0.01 to 0.3
Antioxidant	0 to 2	0 to 0.6

[0045] Various types of sulfur-containing antiwear and/or extreme pressure agents can be used in the practice of the present invention. Examples include dihydrocarbyl polysulfides; sulfurized olefins; sulfurized fatty acid esters of both natural and synthetic origins; trithiones; sulfurized thienyl derivatives; sulfurized terpenes; sulfurized oligomers of C₂-C₈ monoolefins; and sulfurized Diels-Alder adducts such as those disclosed in U.S. reissue patent Re 27,331. Specific examples include sulfurized polyisobutene, sulfurized isobutylene, sulfurized diisobutylene, sulfurized triisobutylene, dicyclohexyl polysulfide, diphenyl polysulfide, dibenzyl polysulfide, dinonyl polysulfide, and mixtures of di-tert-butyl polysulfide such as mixtures of di-tert-butyl trisulfide, di-tert-butyl tetrasulfide and di-tert-butyl pentasulfide, among others. Combinations of such categories of sulfur-containing antiwear and/or extreme pressure agents can also be used, such as a combination of sulfurized isobutylene and di-tert-butyl trisulfide, a combination of sulfurized isobutylene and dinonyl trisulfide, a combination of sulfurized tall oil and dibenzyl polysulfide.

[0046] For purposes of this invention a component which contains both phosphorus and sulfur in its chemical structure is deemed a phosphorus-containing antiwear and/or extreme pressure agent rather than a sulfur-containing antiwear and/or extreme pressure agent.

[0047] Use can be made of a wide variety of phosphorus-containing oil-soluble antiwear and/or extreme pressure additives such as the oil-soluble organic phosphates, organic phosphites, organic phosphonates, organic phosphonites, etc., and their sulfur analogs. Also useful as the phosphorus-containing antiwear and/or extreme pressure additives that may be used in the present invention include those compounds that contain both phosphorus and nitrogen. Phosphorus-containing oil-soluble antiwear and/or extreme pressure additives useful in the present invention include those compounds taught in U.S. Patent Nos. 5,464,549; 5,500,140; and 5,573,696, the disclosures of which are hereby incorporated by reference.

[0048] One such type of phosphorus- and nitrogen-containing antiwear and/or extreme pressure additives which can be employed in the practice of the invention are the phosphorus- and nitrogen-containing compositions of the type described in GB 1,009,913; GB 1,009,914; US 3,197,405 and US 3,197,496. In general, these compositions are prepared by forming an acidic intermediate by the reaction of a hydroxy-substituted triester of a phosphorothioic acid with an inorganic phosphorus acid, phosphorus oxide or phosphorus halide, and neutralizing a substantial portion of said acidic intermediate with an amine or hydroxy-substituted amine. Other types of phosphorus- and nitrogen-containing antiwear and/or extreme pressure additive that may be used in the compositions of this invention include the amine

salts of hydroxy-substituted phosphetanes or the amine salts of hydroxy-substituted thiophosphetanes and the amine salts of partial esters of phosphoric and thiophosphoric acids.

[0049] Some additive components are supplied in the form of solutions of active ingredient(s) in an inert diluent or solvent, such as diluent oil. Unless expressly stated to the contrary, the amounts and concentrations of each additive component are expressed in terms of active additive, i.e., the amount of solvent or diluent that may be associated with such component as received is excluded.

[0050] Commercially available gear additive packages that may be used in the compositions of the present invention include HITEC® 381 Performance Additive, HITEC® 385 Performance Additive and HITEC® 388 Performance Additive, commercially available from Ethyl Corporation. Factors to consider when determining additive selection and level include needs in axle efficiency, trailer tow durability, GL 5 tests, deposit control, seal compatibility, bearing life and limited slip performance.

[0051] The lubricating oil compositions of the present invention may further contain from 0 to 20 weight percent of a seal swell agent. Suitable seal swell agents include hindered polyol esters and oil-soluble diesters. The preferred diesters include the adipates, azelates, and sebacates of C₈-C₁₃ alkanols (or mixtures thereof), and the phthalates of C₄-C₁₃ alkanols (or mixtures thereof). Mixtures of two or more different types of esters (e.g., dialkyl adipates and dialkyl azelates, etc.) can also be used. Examples of such materials include the n-octyl, 2-ethylhexyl, isodecyl, and tridecyl diesters of adipic acid, azelaic acid, and sebacic acid, and the n-butyl, isobutyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, and tridecyl diesters of phthalic acid. Specific examples include di-2-ethylhexyl adipate, di-isooctyl adipate, (2-ethylhexyl)(isodecyl) adipate, di-2-ethylhexyl sebacate and di-isodecyl adipate.

[0052] For certain applications, pour point depressants may be added to the gear oil formulation. If present, the gear oil compositions typically can contain up to 5 wt. % of the pour point depressant.

[0053] Friction modifiers may be included in the gear oil compositions of the present invention. The use of friction modifiers can enhance performance of the gear oils in elastohydrodynamic, mixed and boundary lubricating regimes. The amount of friction modifiers employed in the gear oil compositions of the present invention is preferably in the range of from 0 to 10 wt. %, more preferably 0-5 wt. % and most preferably 0-1.5 wt. %. Suitable friction modifiers for use in the gear oil compositions of the present invention include, but are not limited to, such compounds as fatty amines, alkoxylated fatty amines, borated alkoxylated fatty amines, borated fatty epoxides, aliphatic fatty acid amides, ethoxylated aliphatic ether amines, aliphatic carboxylic acids, aliphatic carboxylic ester-amides, aliphatic phosphonates, aliphatic phosphates, aliphatic thiophosphonates, aliphatic thiophosphates, fatty imidazolines, fatty tertiary amines, fatty phosphites etc., wherein the aliphatic group usually contains at least eight carbon atoms so as to render the compound suitably oil soluble.

[0054] Also suitable are aliphatic substituted succinimides as described in U.S. Patent Nos. 5,021,176; 5,190,680; and RE-34,459 the relevant disclosures of which are herein incorporated by reference. These succinimides are formed by reacting one or more aliphatic succinic acids or anhydrides with ammonia or other primary amines.

[0055] Fatty acid esters of glycerol, such as glycerol monooleate and glycerol tallowate, may be used as the friction modifiers of the present invention. These fatty acid esters may be prepared by a variety of methods well known in the art. The fatty acid esters of glycerol are typically mixtures of from 45% to 55% by weight monoester and from 55% to 45% diester.

[0056] Other preferred friction modifiers include the reaction products of at least one C₅-C₆₀ aliphatic carboxylic acid with at least one amine selected from guanidine, aminoguanidine, urea, thiourea and salts thereof as taught in U.S. Patent No. 4,948,523 incorporated herein by reference for relevant disclosures contained therein. Preferred for use in the present invention are the inorganic salts of aminoguanidine compounds wherein the anion is halide, carbonate, nitrate, phosphate, orthophosphate and the like. Representative of the carboxylic acids useful herein include the commercially available fatty acids or mixtures thereof, derived from sources such as corn oil, soybean oil, palm oil, tung oil, sunflower oil, cottonseed oil, palm kernel oil, olive oil and the like. Particularly preferred are the mono-carboxylic unsaturated fatty acids such as oleic acid. As used herein and in the claims, the term "carboxylic acid" includes the reactive derivatives thereof such as the anhydrides.

[0057] Other preferred friction modifiers include the N-aliphatic hydrocarbyl-substituted diethanol amines and N-aliphatic hydrocarbyl-substituted trimethylene diamines in which the N-aliphatic hydrocarbyl-substituent is at least one straight chain aliphatic hydrocarbyl group free of acetylenic unsaturation and having in the range of about 14 to about 20 carbon atoms; di(hydroxyalkyl) aliphatic tertiary amines in which the hydroxyalkyl groups, being the same or different, each contain from 2 to about 4 carbon atoms, and in which the aliphatic group is an acyclic hydrocarbyl group containing from about 10 to about 25 carbon atoms; hydroxyalkyl aliphatic imidazoline in which the hydroxyalkyl group contains from 2 to about 4 carbon atoms, and in which the aliphatic group is an acyclic hydrocarbyl group containing from about 10 to about 25 carbon atoms as well as mixtures of these friction modifiers. Further details concerning these friction modifiers are set forth in U.S. Pat. Nos. 5,344,579; 5,372,735 and 5,441,656, incorporated herein by reference.

[0058] The multi-grade gear oils of the present invention are particularly suitable for use in automotive gear applications such as final drives, power-dividers or axles in light and heavy-duty vehicles or manual transmissions in a truck

or heavy equipment and Industrial gear applications.

[0059] Preferred finished lubricants for automotive gear applications utilize components proportioned such that the lubricant formulations preferably have an SAE Viscosity Grade of at least SAE 70W, and preferably at least 75W, according to SAE J306 JUL98. Preferred multi-grade ratings include SAE 75W-80, 75W-90 and 80W-140. It is critical that the components used for formulating the lubricant formulations of the present invention are selected such that the formulated oil will not shear out of grade according to SAE J306 requirements when subjected to the 20-hour taper bearing shear test (CEC-L45-T-93). Preferably, the lubricant compositions have a viscosity loss at 100 °C of less than about 15% in the 20-hour taper bearing shear test.

[0060] Preferred finished gear oils of this invention utilize components proportioned such that the kinematic viscosity of the composition at 100 °C according to ASTM D-445 is at least 7.0 cSt and the Brookfield Viscosity (as measured at -55 °C) is less than 150,000 cP.

[0061] Preferred finished gear oils for industrial gear applications utilize components proportioned such that the lubricant formulations have a viscosity classification of ISO 32 or higher according to AGMA 9005-D94.

[0062] In one embodiment, the present invention is directed to a method of reducing sump temperatures in an axle comprising using as the lubricant for said axle a lubricant formulation containing components (B) and (C), wherein the sump temperature of said axle operated using said lubricant formulation is lower than the sump temperature of said axle operated in the same manner and using the same lubricant except that the oil is devoid of at least one of said components (B) and (C).

[0063] The present invention is also directed to a method of increasing the efficiency of an axle comprising using as the lubricant for said axle a lubricant formulation containing components (B) and (C), wherein the efficiency of the axle using said lubricant formulation is increased, as compared to said axle operated in the same manner and using the same lubricant formulation except that the lubricant is devoid of at least one of said components (B) and (C).

EXAMPLES

[0064] Mineral oil based SAE 80W-90 gear oils were prepared comprising 8.25 wt. % of a gear additive package meeting the requirements of API GL-5 and MIL-PRF-2105E, 15 wt. % of a diester seal swell agent, 2 wt. % of a friction modifier and the additional components set forth in the following Table. All of the gear oil formulations contained a hydrotreated 70N mineral oil in an amount to bring the total of all components to 100 wt. %.

[0065] The lubricants were subjected to a cycling test to simulate various conditions that a gear oil may experience and the results are set forth in Table 1. The sequences differed in the speed and/or torque applied to the axle. Highway driving conditions were simulated using a high speed and low load, city and severe driving conditions were simulated using low speed/high load and medium speed/high load respectively. The axle sump temperatures were measured and the axle efficiency was calculated for each sequence. It is desirable to have low axle sump temperatures and high axle efficiency values.

Table 1

	1*	2*	3	4
PIB¹	20	4.5		
OCP		11.5 ⁴	17 ³	11.5 ⁴
PAO²	10		10	10
Highway T(°F)/Eff.	DNT	130/87.27	143/89.78	140/89.87
City T(°F)/Eff.	DNT	206/96.22	181/97.38	179/97.30
Severe T(°F)/Eff.	223/97.37	215.8/97.21	198/98.19	198/98.20

* Comparative Examples

DNT Did Not Test sample for Axle Temperature or Axle Efficiency

¹ Polyisobutene having a number average molecular weight of approximately 2145

² 100 cSt hydrogenated polyalphaolefin

³ Ethylene-propylene copolymer having an ethylene content of approximately 55 mol. % and a kinematic viscosity at 100 °C of approximately 500 cSt.

⁴ Ethylene-propylene copolymer having an ethylene content of approximately 43 mol. % and a kinematic viscosity at 100 °C of approximately 2100 cSt.

[0066] It is clear, upon examination of the above Table, that the compositions of the present invention (Examples 3 and 4) exhibit improved (lower) axle temperatures and improved (higher) axle efficiencies compared to mineral oil based compositions outside the scope of the present invention (Comparative Examples 1 and 2).

[0067] This invention is susceptible to considerable variation in its practice. Accordingly, this invention is not limited to the specific exemplifications set forth hereinabove. Rather, this invention is within the spirit and scope of the appended claims, including the equivalents thereof available as a matter of law.

[0068] The patentee does not intend to dedicate any disclosed embodiments to the public, and to the extent any disclosed modifications or alterations may not literally fall within the scope of the claims, they are considered to be part of the invention under the doctrine of equivalents.

[0069] Typically, references in this specification to "Viscosity Index" are to Viscosity Index as calculated according to ASTM D2270.

[0070] Typically, the gear additive package (D) comprises (i) a sulfur and phosphorus containing anti-wear or extreme pressure additive, (ii) an antioxidant, (iii) a corrosion inhibitor, (iv) an antifoam additive and, optionally, (v) an ashless dispersant. Typically, when the gear additive package contains these ingredients, the lubricant composition satisfies the API GL-5 performance requirements, which are published in ASTM Publication STP-512A entitled "Laboratory Performance Tests for Automotive Gear Lubricants" (March 1987).

[0071] Typically, the lubricant composition of the invention is suitable for use in a nonsynchronised manual transmission such as, for example, a manual transmission for a bus or truck. Typically, such lubricant compositions satisfy the API MT-1, or D-5760-95, performance requirements. Accordingly, further preferred gear additive packages are those which enable the lubricant to satisfy the performance requirements set out in ASTM designation D-5760-95, as published October 1995.

[0072] Further preferred gear additive packages are those which enable the lubricant to meet the SAE J2360 performance requirements, as published in November 1998. These are equivalent to the MIL-PRF-2105 performance requirements.

[0073] Further preferred gear oil additive packages are those which enable the lubricant to meet the performance requirements for any of the AGMA grades, as set out in AGMA 9005-D94, approved on 1 August 1994, for a compounded or non-compounded R & O gear lubricant, an extreme pressure gear lubricant or a synthetic gear lubricant.

[0074] Typically, the lubricant composition of the invention has an SAE viscosity grade of 70W or higher according to SAE J306 JUL98 (as revised July 1998). The viscometric properties of oils with an SAE viscosity grade of 70W or higher are shown in the Table below.

SAE Viscosity Grade	Maximum temperature for viscosity of 150,000 cP, °C	Kinematic viscosity at 100°C, cSt (minimum)	Kinematic viscosity at 100°C, cSt (maximum)
70W	-55	4.1	-
75W	-40	4.1	-
80W	-26	7.0	-
85W	-12	11.0	-
80	-	7.0	<11.0
85	-	11.0	<13.5
90	-	13.5	<24.0
140	-	24.0	<41.0
250	-	41.0	

[0075] The Brookfield viscosity of 150,000 cP (150,000 mPa s⁻¹) can be determined, for example, according to ASTM D-2983. The kinematic viscosity at 100°C can be determined, for example, according to ASTM D445.

[0076] Further preferred lubricant compositions of the invention have an ISO viscosity grade of 32 or higher, according to AGMA 9005-094, as approved on 1 August 1994. The viscometric properties of such oils are shown in the Table below.

Viscosity range, mm ² /s (cSt) at 40°C	Equivalent ISO grade
28.8 to 35.2	32
41.4 to 50.6	46
61.2 to 74.8	68
90 to 110	100

(continued)

Viscosity range, mm ² /s (cSt) at 40°C	Equivalent ISO grade
135 to 165	150
198 to 242	220
288 to 352	320
414 to 506	460
612 to 748	680
900 to 1100	1000
1350 to 1650	1500

[0077] Typically, said 20-hour taper bearing shear test is the test set out in CEC test method L-45-T-93, entitled "Viscosity Shear Stability of Transmission Lubricants (KRL - Tapered Roller Bearing Test Rig) Shear Stability Test, 1993". Typically, components (B) and (C) are selected such that the formulated oil has a kinematic viscosity at 100°C of at least 4.1, more typically at least 7.0, preferably at least 11.0, when subjected to said 20- hour taper bearing shear test.

Claims

1. A lubricant composition suitable for use as an automotive or industrial gear lubricant comprising:

- (A) from about 40 to about 70 wt. %, based on the total weight of the lubricant composition, of a mineral oil;
- (B) from about 2 to about 20 wt. %, based on the total weight of the lubricant composition, of at least one selected from vinyl aromatic-diene copolymers, olefin copolymers and mixtures thereof;
- (C) from about 2 to about 20 wt. %, based on the total weight of the lubricant composition, of at least one polyalphaolefin having a kinematic viscosity of at least 40 cSt at 100°C; and
- (D) from about 3 to about 20 wt. %, based on the total weight of the lubricant composition, of a gear additive package;

wherein the lubricant composition has a Viscosity Index of greater than 140.

2. A composition according to claim 1 wherein component (B) is a vinyl aromatic-diene copolymer.

3. A composition according to claim 2 wherein component (B) is a copolymer of styrene and at least one conjugated diene selected from butadiene and isoprene.

4. A composition according to claim 3 wherein the copolymer is hydrogenated.

5. A composition according to claim 1 wherein component (B) is an olefin copolymer.

6. A composition according to claim 5 wherein component (B) is a copolymer of ethylene and at least one C₃-C₁₂ alpha-olefin.

7. A composition according to claim 6 wherein the copolymer further comprises a non-conjugated polyene.

8. A composition according to any one of the preceding claims, wherein the gear additive package comprises at least one selected from dispersants, corrosion inhibitors, extreme pressure additives, anti-wear additives, rust inhibitors, antioxidants, deodorizers, defoamers, demulsifiers, dyes, friction modifiers and fluorescent coloring agents.

9. A composition according to any one of the preceding claims further comprising from 0 to 20 wt. %, based on the total weight of the lubricant composition, of at least one seal swell agent and/or from 0 to 5 wt. %, based on the total weight of the lubricant composition, of a pour point depressant.

10. A composition according to any one of the preceding claims, wherein the gear additive package is such that the lubricant satisfies the API GL-5 performance requirements, and/or the API MT-1 performance requirements, and/or the MIL-PRF-2105E performance requirements, and/or the AGMA 9005-D94 performance requirements.
- 5 11. A composition according to any one of the preceding claims, wherein the mineral oil has a viscosity index greater than 80 and contains less than 0.03 wt. % sulfur.
12. A composition according to claim 11, wherein the mineral oil has a viscosity index of at least 110.
- 10 13. A composition according to claim 12, wherein the mineral oil comprises at least one selected from Group II oils, Group III oils and mixtures thereof.
14. A composition according to any one of the preceding claims, which has an SAE Viscosity Grade of 70W or higher according to SAE J306 JUL 98 and/or an ISO Viscosity Grade of 32 or higher according to AGMA 9005-D94.
- 15 15. A composition according to any one of the preceding claims wherein components (B) and (C) are selected such that the formulated oil will not shear out of grade according to SAE J306 requirements when subjected to a 20-hour taper bearing shear test.
- 20 16. A method of reducing the sump temperature in an axle, which method comprises lubricating said axle with a lubricant composition according to any one of the preceding claims, wherein the sump temperature of said axle lubricated with said lubricant composition is reduced, as compared to the sump temperature of said axle operated in the same manner and lubricated with the same lubricant composition except that the lubricant composition is devoid of at least one of components (B) or (C).
- 25 17. A method of increasing the efficiency of an axle which method comprises lubricating said axle with a lubricant composition according to any one of the preceding claims, wherein the efficiency of the axle lubricated with said lubricant composition is increased, as compared to said axle operated in the same manner and lubricated with the same lubricant composition except that the lubricant composition is devoid of at least one of components (B) and (C).
- 30 18. Use of an additive comprising:

 (B) at least one vinyl aromatic-diene copolymer as defined in any one of claims 1 to 4 and/or at least one olefin copolymer as defined in any one of claims 1 and 5 to 7; and
 (C) at least one polyalphaolefin having a kinetic viscosity of at least 40cSt at 100°C,

 to reduce the sump temperature and/or to increase the efficiency of an axle, when present in a lubricant composition according to any one of claims 1 to 15 in the axle.
- 40 19. Use of a composition according to any one of claims 1 to 15, to lubricate a gear or a transmission.